

Demicheleite-(I), BiSI, a new mineral from La Fossa Crater, Vulcano, Aeolian Islands, Italy

F. DEMARTIN*, C. M. GRAMACCIOLI AND I. CAMPOSTRINI

Università degli Studi di Milano, Dipartimento di Chimica Strutturale e Stereochimica Inorganica, via G. Venezian 21, I-20133 Milano, Italy

[Received 27 January 2010; Accepted 24 March 2010]

ABSTRACT

Demicheleite-(I), ideally BiSI, is the iodine-dominant analogue of demicheleite-(Br) and demicheleite-(Cl). It was found in an active medium-temperature intracrater fumarole at La Fossa crater, Vulcano Island, Aeolian archipelago, Sicily, Italy. The mineral is the first bismuth sulphiodide so far discovered in a wholly natural environment, and corresponds to the already known synthetic compound. It occurs as acicular to stout, translucent crystals up to 0.25 mm long in an altered pyroclastic breccia, together with demicheleite-(Br), bismoclite, bismuthinite, godovikovite, panichiite, aiolosite, brontesite, adranosite and other new phases under study. The colour is dark red to black, the lustre submetallic. The unit cell is orthorhombic, space group $Pnam$, with $a = 8.4501(7)$ Å, $b = 10.1470(9)$ Å, $c = 4.1389(4)$ Å, $V = 354.88(4)$ Å³, and $Z = 4$. The crystal habit is prismatic, with the main forms {110} and {111} inferred from analogy with demicheleite-(Br). Twinning was not observed. The strongest 6 lines in the X-ray powder diffraction pattern [$d_{\text{obs.}}(\text{Å})$ (hkl)] are: 6.490 (100) (110); 4.346 (94) (120); 3.896 (90) (210); 2.709 (60) (310); 2.161 (38) (330); 3.243 (22) (220). The chemical analysis obtained by WDS electron microprobe gave: Bi 58.32, S 9.43, I 23.69, Br 5.66, Cl 1.01, totalling 98.11 wt.%, corresponding to an empirical formula (based on 3 a.p.f.u.) of: $\text{Bi}_{0.97}\text{S}_{1.03}(\text{I}_{0.65}\text{Br}_{0.25}\text{Cl}_{0.10})_{\Sigma 1.00}$. The unit-cell data are close to those of the synthetic compound, whose crystal structure is already known. The calculated density is 6.411 g cm^{-3} .

KEYWORDS: demicheleite-(I), demicheleite-(Br), demicheleite-(Cl), new mineral species, bismuth, iodine minerals, sulphiodides, Vulcano Island, Aeolian Islands, Italy.

Introduction

In the last few years, a considerable number of new species have been discovered at La Fossa crater, Vulcano, Aeolian Islands, during a systematic investigation of the fumarolic products of that locality (see Campostrini *et al.*, 2008; Demartin *et al.*, 2008a,b,c, 2009a,b,c, 2010a,b, and references therein).

Here, we report the discovery of the new mineral demicheleite-(I), BiSI. It is the natural equivalent of bismuth sulphide iodide, a substance

belonging to a well known group of synthetic thiohalogenides which have drawn much attention because of their optical, photoconducting and ferroelectric properties (Doenges, 1950; Haase-Wessel, 1973; Voutsas and Rentzperis, 1980, 1984, and references therein). The Br and Cl equivalents, demicheleite-(Br), BiSBr, and demicheleite-(Cl), BiSCL respectively, were previously discovered in the same environment (Demartin *et al.*, 2008c, 2009b). After mutnovskite, $\text{Pb}_4\text{As}_2\text{S}_6\text{ICl}$ (Zelenski *et al.*, 2006; Bindi *et al.*, 2008), demicheleite-(I) is the second known mineral of fumarolic origin that contains iodine as an essential constituent.

The mineral is named as the iodine-analogue of demicheleite-(Br) and demicheleite-(Cl). Both the mineral and the mineral name have been approved

* E-mail: francesco.demartin@unimi.it
DOI: 10.1180/minmag.2010.074.1.141

by the IMA Commission on New Minerals, Nomenclature and Classification (CNMNC) (No. 2009-049). The holotype is deposited (No. 2009-02) in the Reference Collection of Dipartimento di Chimica Strutturale e Stereochimica Inorganica of Università degli Studi di Milano.

Occurrence and physical properties

The new mineral demicheleite-(I) occurs in a medium-temperature ($\approx 250^\circ\text{C}$) intracrater fumarole on altered pyroclastic breccia, as acicular to stout, nearly black crystals up to 0.25 mm long, accompanied by demicheleite-(Br), bismoclite, bismuthinite and aiolosite (Demartin *et al.*, 2010a). In addition, in the same or similar environments, very unusual species containing ammonium are present, such as godovikovite, $(\text{NH}_4)\text{Al}(\text{SO}_4)_2$, adranosite, $(\text{NH}_4)_4\text{NaAl}_2(\text{SO}_4)_4\text{Cl}(\text{OH})_2$ (Demartin *et al.*, 2010b), pyracmonite, $(\text{NH}_4)_3\text{Fe}(\text{SO}_4)_3$ (Demartin *et al.*, 2010c), and a number of other new phases, some of which are still under investigation. Some of these phases, e.g. panichiite, $(\text{NH}_4)_2\text{SnCl}_6$, brontesite, $(\text{NH}_4)_3\text{PbCl}_5$ (Demartin *et al.*, 2009a,c) and $(\text{NH}_4)_7\text{Bi}_3\text{Cl}_{16}$ are chloride complexes, and as well as ammonium, also contain heavy metals such as Sn, Pb and Bi. The presence of a considerable activity of volatile

metal chlorides and especially of free ammonia in the gas prevents the dissociation of such complexes even at moderately high temperature.

The crystal habit is prismatic, with prevailing forms $\{110\}$ and $\{111\}$ and is very similar to that of demicheleite-(Br) (Fig. 1). The colour is dark red to black, the streak is brown; the lustre submetallic. The mineral is not fluorescent. It is brittle and cleavage was not observed. The calculated density is 6.411 g cm^{-3} (from the empirical formula reported below and the unit-cell data). The indices of refraction could not be determined using the immersion method because they are too high and the crystals are sensitive to chemical agents.

Chemical data

Chemical analyses were carried out by means of a JEOL JXA 8200 electron microprobe (in WDS mode using an accelerating potential of 15 kV, a probe current of $5 \times 10^{-9}\text{ A}$ and final beam diameter of $10\ \mu\text{m}$). The analytical results are reported in Table 1. The empirical formula (based on 3 a.p.f.u.) is: $\text{Bi}_{0.97}\text{S}_{1.03}(\text{I}_{0.65}\text{Br}_{0.25}\text{Cl}_{0.10})_{\Sigma 1.00}$; the simplified formula is therefore BiSI, which requires: Bi 56.80, S 8.71, I 34.49, totalling 100.00 wt.%. Although iodine clearly prevails over the other halogens, the natural sample here studied contains 25% Br and 10% Cl (in atoms).

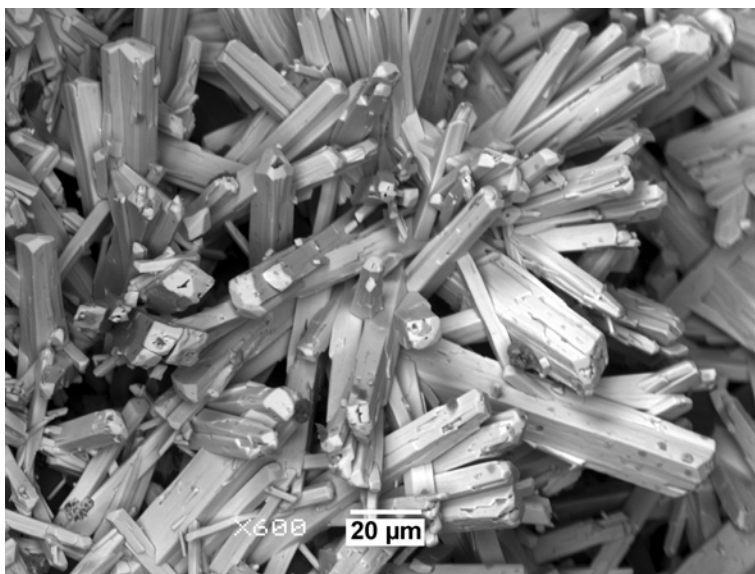


FIG. 1. Scanning electron microscope (SEM) image (BSE) of demicheleite-(I).

DEMICHELEITE-(I) BiSI, A NEW MINERAL

TABLE 1. Chemical composition of demicheleite-(I).

Constituent	Wt.%	Range	Standard deviation	Probe Standard
Bi	58.32	57.38–58.88	0.7	Bi ₂ Se ₃
S	9.43	9.21–9.63	0.4	PbS
I	23.69	21.28–25.09	0.3	KIO ₃
Br	5.66	4.97–7.21	0.4	TlBr
Cl	1.01	0.50–1.34	0.2	Scapolite
Total	98.11			

Therefore, the new mineral could also be considered as an intermediate between BiSI and the isostructural sulphide bromide, BiSBr or sulphide chloride BiSCl (Voutsas and Rentzeperis, 1980, 1984).

TABLE 2. X-ray powder diffraction data for demicheleite-(I) and a comparison with synthetic BiSI*.

	<i>I</i> / <i>I</i> ₀	<i>d</i> _{obs.} (Å)	<i>d</i> _{calc.} (Å)	BiSI	<i>h k l</i>
	100	6.490	6.493	6.565	1 1 0
	3	5.069	5.073	5.131	0 2 0
	94	4.346	4.350	4.398	1 2 0
	20	4.234	4.225	4.259	2 0 0
	90	3.896	3.900	3.934	2 1 0
	12	3.835	3.832	3.866	0 1 1
	8	3.505	3.490	3.523	1 1 1
	22	3.243	3.247	3.277	2 2 0
	3	3.145	3.140	3.174	1 3 0
	22	2.999	2.998	3.028	1 2 1
	9	2.965	2.957	2.981	2 0 1
	6	2.839	2.839	2.863	2 1 1
	60	2.709	2.714	2.736	3 1 0
	15	2.643	2.640	2.667	2 3 0
	11	2.621	2.619	2.646	0 3 1
	19	2.537	2.537	2.565	0 4 0
	9	2.504	2.502	2.527	1 3 1
	21	2.466	2.463	2.484	3 2 0
	8	2.426	2.430	2.458	1 4 0
	4	2.268	2.270	2.288	3 1 1
	38	2.161	2.164	2.184	3 3 0
	9	2.123	2.116	2.133	3 2 1
	7	2.100	2.095	2.117	1 4 1
	5	2.072	2.069	2.088	0 0 2
	5	1.974	1.972	1.989	1 1 2
	7	1.955	1.950	1.966	4 2 0
	6	1.915	1.918	1.935	3 3 1
	7	1.848	1.850	1.865	4 1 1
	9	1.825	1.828	1.844	2 1 2
	3	1.747	1.745	1.760	2 2 2
	3	1.714	1.715	1.732	3 4 1
	6	1.657	1.658	1.677	1 6 0
	5	1.624	1.623	1.638	4 4 0
	5	1.604	1.603	1.616	5 2 0

* PDF file (00-043-0652)

X-ray data

No single crystals suitable for accurate structure refinement were found. X-ray powder-diffraction data, obtained using a Philips PW1830 diffractometer, with Cu-K α radiation ($\lambda = 1.5405 \text{ \AA}$) (Table 2), fit the orthorhombic space group *Pnam*, and the unit-cell parameters $a = 8.4501(7) \text{ \AA}$, $b = 10.1470(9) \text{ \AA}$ and $c = 4.1389(4) \text{ \AA}$, $V = 354.88(4) \text{ \AA}^3$, obtained with the program *UNITCELL* (Holland and Redfern, 1997). As expected, in view of the presence of significant amounts of the lighter halogens (Cl and Br), the unit-cell volume (Table 3) is significantly smaller than that of the pure compound BiSI (Haase-Wessel, 1973). A detailed discussion of the crystal structure of the bismuth sulphohalides BiSX ($X = \text{Cl, Br, I}$) together with those of related compounds is reported, for instance, in Keller and Krämer (2006).

Discussion

The discovery in nature of the iodine-rich equivalent of the bismuth minerals demicheleite-(Br) and demicheleite-(Cl) increases the number of natural sulphohalides, most of which are Ag- or Hg- rather than Bi-bearing minerals, as for instance corderoite, Hg₃S₂Cl₂ (Foord *et al.*, 1974), lavrentievite, Hg₃S₂Cl₂ and arzakite, Hg₃S₂Br₂ (Vasil'ev *et al.*, 1984), perrouditite, Ag₄Hg₅S₅(I,Br)₂Cl₂ (Sarp *et al.*, 1987) and capgaronnite, AgHgClS (Mason *et al.*, 1992).

TABLE 3. Unit-cell parameters for demicheleite minerals and their synthetic equivalents.

	Demicheleite-(I) BiSI*	Demicheleite-(Br) BiSBr [†]	Demicheleite-(Cl) BiSCL [‡]	BiSI [#]	BiSBr [§]	BiSCL [¶]
<i>a</i> (Å)	8.4501(7)	8.0424(9)	7.802(1)	8.519(5)	8.1666(9)	7.7508(16)
<i>b</i> (Å)	10.1470(9)	9.8511(11)	9.930(1)	10.177(8)	9.8532(9)	9.9920(5)
<i>c</i> (Å)	4.1389(4)	4.0328(5)	3.9905(6)	4.172(6)	4.0492(6)	3.9955(5)
<i>V</i> (Å ³)	354.88(4)	319.50(6)	309.16(8)	361.70(6)	325.83(7)	309.44(8)

* This work; [†] Demartin *et al.*, 2008c; [‡] Demartin *et al.*, 2009b; [#] Haase-Wessel (1973); [§] Voutsas and Rentzeperis (1984); [¶] Voutsas and Rentzeperis (1980).

Sulphochlorides or halogen-bearing sulphosalts of Bi and/or Pb (such as Bi₁₉Cl₃S₂₇ and Pb₄SCL₆) were already observed by Garavelli *et al.* (1997, 2005) in quartz tubes inserted into the outlet of fumaroles of La Fossa crater, Vulcano, at temperatures from 300 to 500°C. According to these authors (and following the long list of references reported in these works), the deposition of such sulphohalides is due to reaction of PbCl₂ (cotunnite) with H₂S or galena. Similar reactions occur in the formation of bismuth sulphochlorides from BiCl₃ and H₂S. A bismuth sulphoiodide BiS(I,Cl,Br) which might be related to demicheleite-(I) was also observed as a component of volcanic sublimates collected in quartz tubes at the Mutnovsky volcano, Kamchatka, Russia (Zelenski and Bortnikova, 2005). All these observations underline the chemical complexity of such volcanic environments, which are currently the object of active interest.

A significant enrichment in the heavier halogens, which is particularly rare in nature, does not seem to be unusual in volcanic sublimates at Vulcano, and is similar to what occurs at the Mutnovsky volcano. Such process may lead to the formation of new phases, where Br or I prevail over Cl (Demartin *et al.*, 2008c, 2009a,b, and references therein). In the same fumarolic system where demicheleite-(I) was found, other phases rich in the heavier halogens are also present, such as TII, TIBr and a TI-Bi iodide currently under investigation.

Acknowledgements

The authors are indebted to Mr Andrea Risplendente for assistance in the microprobe analysis. Suggestions from the referees among whom was Dr Anthony Kampf are highly appreciated.

References

- Bindi, L., Garavelli, A., Pinto, D., Pratesi, G. and Vurro, F. (2008) Ordered distribution of I and Cl in the low-temperature crystal structure of mutnovskite, Pb₄As₂S₆ICl: An X-ray single-crystal study. *Journal of Solid State Chemistry*, **18**, 306–312.
- Campostrini, I., Demartin, F., Gramaccioli, C.M. and Orlandi, P. (2008) Hephaistosite, TIPb₂Cl₅, a new thallium mineral species from La Fossa crater, Vulcano, Aeolian Islands, Italy. *The Canadian Mineralogist*, **46**, 701–708.
- Demartin, F., Gramaccioli, C.M., Campostrini, I. and Orlandi, P. (2008a) Knasibfite, K₃Na₄[SiF₆]₃[BF₄], a new hexafluorosilicate-tetrafluoroborate from La Fossa crater, Vulcano, Aeolian Islands, Italy. *The Canadian Mineralogist*, **46**, 419–425.
- Demartin, F., Gramaccioli, C.M., Campostrini, I. and Orlandi, P. (2008b) Thermessaite K₂[AlF₃SO₄], a new ino-alumino-fluoride-sulfate from La Fossa crater, Vulcano, Aeolian Islands, Italy. *The Canadian Mineralogist*, **46**, 693–700.
- Demartin, F., Gramaccioli, C.M., Campostrini, I. and Orlandi, P. (2008c) Demicheleite, BiSBr, a new mineral from La Fossa crater, Vulcano, Aeolian Islands, Italy. *American Mineralogist*, **93**, 1603–1607.
- Demartin, F., Campostrini, I. and Gramaccioli, C.M. (2009a) Panichiite, natural ammonium hexachlorostannate, (NH₄)₂SnCl₆, from La Fossa crater, Vulcano, Aeolian Islands, Italy. *The Canadian Mineralogist*, **47**, 367–372.
- Demartin, F., Gramaccioli, C.M. and Campostrini, I. (2009b) Demicheleite-(Cl), BiSCL, a new mineral from La Fossa Crater, Vulcano, Aeolian Islands, Italy. *American Mineralogist*, **94**, 1045–1048.
- Demartin, F., Gramaccioli, C.M. and Campostrini, I. (2009c) Brontesite, (NH₄)₃PbCl₅, a new product of fumarolic activity from La Fossa Crater, Vulcano, Aeolian Islands, Italy. *The Canadian Mineralogist*, **47**, 1237–1243.
- Demartin, F., Gramaccioli, C.M. and Campostrini, I.

DEMICHELEITE-(I) BiSI, A NEW MINERAL

- (2010a) Aiolosite, $\text{Na}_2(\text{Na}_2\text{Bi})(\text{SO}_4)_3\text{Cl}$, a new sulfate isotypic to apatite from La Fossa Crater, Vulcano, Aeolian Islands, Italy. *American Mineralogist*, **95**, 382–385.
- Demartin, F., Gramaccioli, C.M. and Campostrini, I. (2010b) Adranosite, $(\text{NH}_4)_4\text{NaAl}_2(\text{SO}_4)_4\text{Cl}(\text{OH})_2$, a new ammonium sulfate chloride from La Fossa Crater, Vulcano, Aeolian Islands, Italy. *The Canadian Mineralogist*, **48**, in press.
- Demartin, F., Gramaccioli, C.M. and Campostrini, I. (2010c) Pyracmonite, $(\text{NH}_4)_3\text{Fe}(\text{SO}_4)_3$, a new ammonium iron sulfate from La Fossa crater, Vulcano, Aeolian Islands, Italy. *The Canadian Mineralogist*, (in press).
- Doenges, E. (1950) Über Thiohalogenide des dreiwertigen Antimons und Wismuts. *Zeitschrift für Anorganische und Allgemeine Chemie*, **263**, 112–132.
- Foord, E.E., Berendsen, P. and Storey, L.O. (1974) Corderoite, first natural occurrence of $\alpha\text{-Hg}_3\text{S}_2\text{Cl}_2$, from the Cordero mercury deposit, Humboldt County, Nevada. *American Mineralogist*, **59**, 652–655.
- Garavelli, A., Laviano, R. and Vurro, F. (1997) Sublimate deposition from hydrothermal fluids at the Fossa crater - Vulcano, Italy. *European Journal of Mineralogy*, **9**, 423–432.
- Garavelli, A., Mozgova, N.N., Orlandi, P., Bonaccorsi, E., Pinto, D., Močlo, Y. and Borodaev, Yu.S. (2005) Rare sulfosalts from Vulcano, Aeolian Islands, Italy. VI. Vurroite $\text{Pb}_{20}\text{Sn}_2(\text{Bi,As})_{22}\text{S}_{54}\text{Cl}_6$, a new mineral species. *The Canadian Mineralogist*, **43**, 703–711.
- Haase-Wessel, W. (1973) Die Kristallstruktur des Wismutsulfidjodids (BiSJ). *Naturwissenschaften*, **60**, 474.
- Holland, T.J.B. and Redfern, S.A.T. (1997) Unit cell refinement from powder diffraction data: the use of regression diagnostics. *Mineralogical Magazine*, **61**, 65–77.
- Keller, E. and Krämer, V. (2006) Experimental versus expected halide-ion size differences; structural changes in three series of isotypic bismuth chalcogenide halides. *Acta Crystallographica B*, **62**, 417–423.
- Mason, B., Mumme, W.G. and Sarp, H. (1992) Capgaronnite, $\text{HgS}\cdot\text{Ag}(\text{Cl,Br,I})$, a new sulfide-halide mineral from Var, France. *American Mineralogist*, **77**, 197–200.
- Sarp, H., Birch, W.D., Hlava, P.F., Pring, A., Sewell, D.K.B. and Nickel, E.H. (1987) Perroudite, a new sulfide-halide of Hg and Ag from Cap Garonne, Var, France, and from Broken Hill, New South Wales, and Coppin Pool, Western Australia. *American Mineralogist*, **72**, 1251–1256.
- Vasil'ev, V.L., Pal'chik, N.A. and Grechishev, O.K. (1984) Lavrentievite and arzakite, new natural sulfohalogenides of mercury. *Geologiya i Geofizika*, **7**, 54–63. (in Russian).
- Voutsas, G.P. and Rentzeperis, P.J. (1980) The crystal structure of the paraelectric bismuth thiochloride, BiSCl , *Zeitschrift für Kristallographie*, **152**, 109–118.
- Voutsas, G.P. and Rentzeperis, P.J. (1984) The crystal structure of bismuth sulfide bromide, BiSBr , *Zeitschrift für Kristallographie*, **166** 153–158.
- Zelenski, M. and Bortnikova, S. (2005) Sublimate speciation at Mutnovsky volcano, Kamchatka. *European Journal of Mineralogy*, **17**, 107–118.
- Zelenski, M., Balić-Žunić, T., Bindi, L., Garavelli, A., Makovický, E., Pinto, D. and Vurro, F. (2006) First occurrence of iodine in natural sulfosalts: The case of mutnovskite, $\text{Pb}_2\text{AsS}_3(\text{I,Cl,Br})$, a new mineral from Mutnovsky volcano, Kamchatka Peninsula, Russian Federation. *American Mineralogist*, **91**, 21–28.

